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U.S. Environmental Protection Agency
CLP Sample Management Office
P.O. Box 818, Alexandria, Virginia 22313
PHONE: (703)/557-2490 or FTS/557-2490

SAS Number

7084E

SPECIAL ANALYTICAL SERVICES
Client Request

☐ Regional Transmittal☐ Telephone Request

A. EPA Region/Client: Region V/ARCS, E & E
B. RSCC Representative: Jan Pels
C. Telephone Number: (312)353-2720
Date of Request: 2/7/92
Site Name: NL Industries, TaraCorp Lead Smelt Site, Granite City, IL K7

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested:

Analysis of cadmium and lead by graphite furnace atomic absorption (GFAA) of bulk dust from private residences, for those samples with small aliquot weights. Results must be reported as mg/kg cadmium or lead on an as received basis. Total solids is not to be determined for these samples. Sample weights must be recorded for each sample as received (see ICP SAS). Note and record the character of each sample. Analyze any suspected paint chips (if present) separately from the dust. The separation and description of the samples is extensively described in the ICP SAS and must be followed for this GFAA SAS. The dust portion of the sample must contain dust and lint (hair, carpet fibers, etc.) after grinding. Only the dust will be subsampled for digestion and analysis. Report individual and composite values for Cd and Pb. Examples of completed Form 1 reports and a blank Form 1 are included as an attachment to this SAS. The laboratory must also include a detailed case narrative with the deliverable package. This case narrative must describe any problems that were encountered during sample preparation and analysis. Any unusual sample characteristics must also be included to assist the Regional validation of the sample packages. An example of a case narrative is also include in the attachments.

2. Definition and number of work units involved: 355 dust samples - (see ICP SAS)

Cd ad Pb analyses must be performed by GFAA for dust or suspected paint chip samples with aliquot sizes less than 1.0 g, which is insufficient for ICP emission spectroscopy analysis (1 g aliquot digested into 200 mls final volume). If the

sample aliquot size is small (or if the sample aliquot size is small when ICP analysis requires reanalysis), 50-100 mg of dust must be digested into a final 200 ml volume. GFAA serves as a back-up to the preferred ICP method. The sample separation, description and preparation procedures are described in great detail in the ICP SAS (sections 1, 2 and 7) and must be followed for this SAS. The only exceptions to this are the special procedures detailed in this SAS for samples with very small aliquot sizes.

The procedures outlined in this SAS are labor intensive and the laboratory is cautioned to read this SAS carefully prior to submitting a bid. The laboratory can expect that 50% of the samples will contain suspected paint chips. SMO and the Region may initiate a conference phone call with the selected laboratory to assure that all parties understand the scope and expectations for this project. SMO and Region 5 may also visit the laboratory during the initial analyses to audit compliance with the analytical specifications, to provide corrective actions, and to minimize problems associated with subsequent data validations.

3. Purpose of analysis:

Superfund ATSDR Multi-State Lead Exposure Study

4. Estimated date(s) of collection: September 4 - October 4, 1991

5. Estimated date(s) and method of shipment: Federal Express - upon award of SAS.

6. * Laboratory data rejection and nonpayment will be recommended if the methods outlined in this SAS are not followed by the laboratory.* The number of days analysis and data required after laboratory receipt of samples: _____

Data due 35 days from receipt of samples.

7. Analytical protocol required:

Sample description and preparation procedures are described in the ICP SAS for Cd and Pb in dust. Record the total sample weight on Form 1. The samples must be homogenized in a SPEX 8000 Mixer or equivalent. Paint chip samples with a total sample weight less than 100 mg must not be homogenized prior to digestion. For paint chip samples containing less than 100 mg, the entire sample must be digested. Samples must be digested using SOW 7/88 or ILM01. GFAA standards and sample digests must be matrix matched as to the final acid concentrations. 50 to 100 mg sample aliquots must be digested to a final volume of 200 mls. Very small samples (5-50 mg) may be digested and brought to final volumes of 50 to 100 ml, but the acid concentrations must be the same as the other samples and standards. All final digest volumes must be carefully documented and recorded in the raw data in the case. If any samples contain significant amounts of paint chips, these must be separated into dust and paint chip portions. Each portion must be analyzed separately and results must be reported for individual portions as well as for a mathematical composite value (by weight).

Instrumental analysis will be Method 213.2 CLP-M* (Atomic Absorption, Furnace Technique) for Cd and Method 239.2 CLP-M* (Atomic Absorption, Furnace Technique) for Pb. High levels of background and interference can be expected for the paint chip samples and at moderate levels for the dust samples. In order to minimize the interferences, only instruments with Zeeman or Smith-Hieftje background correction

systems may be used. Deuterium background is not to be used. No exceptions for deuterium background will be granted.

→ * Laboratories must supply the instrument operating conditions including instrument manufacturer, model, temperature program, matrix modifiers, tube type (pyrolytic, platform, etc), instrument detection limits and injection volumes with the bids that are submitted to SMO. * *

Analytical spikes must be performed on all samples. A spike level of 20 ug/l for Pb and 1 or 2 ug/l for Cd (depending on the linear range of the instrument). Additional technical considerations are listed in item #8.

8. Special technical instruction:

The Graphite Furnace Decision Tree in SOW 7/88 of ILM01 must be used by the laboratory with the following exceptions. When dilutions are required for samples with high concentrations of Cd or Pb, the dilution factor chosen should not yield a sample concentration that is less than 25% of the largest standard in the calibration curve. Duplicate injections and analytical spikes are required. If the analytical spike recovery is out side of the range of 80%-120%, the sample must be rerun. If the analytical spike recovery is out of control (Pb > 10 ug/l and Cd > 1 ug/l), the laboratory must follow the GFAA decision tree. If the analytical spike recovery is out of control (Pb < 10 ug/l and Cd < 1 ug/l), the sample should be diluted 1:2 and rerun. If the analytical spike is still out of control, the sample must be run by MSA as per the decision tree. If problems occur, the laboratory must contact SMO and Region V.

9. Analytical results required:

ILM01 deliverables must be provided. All forms and raw data must be original (as much as possible). The IDLs must be less than 0.5 ug/l Cd and less than 5 ug/l Pb. These will be the CRDLs for this study and all values equal to or greater than IDL are to be reported as per ILM01.

10. Other

Examples of Form 1, sample weight logs, and sample description logs are included as attachments. Their use is mandatory. The information included on these forms must be included in the raw data, along with all other SOW required forms and deliverables.

11. Name of sampling/shipping contact: Cathy Kouris, E & E
Phone: (312)663-9415

12. Data Requirements

<u>Parameter:</u>	<u>Detection Limit</u>	<u>Precision Required</u> (±% or conc.)
Cd	0.5 ug/l in digest (or 2 ppm in the dust for a 50 mg aliquot) Report Concentration down to specific IDL used	30% RPD in duplicate samples greater than 10 mg/kg or a duplicate difference <2 mg/kg for results less than 10 mg/kg.
Pb	5 ug/l in the digest (or 20 ppm in dust for aliquot)	30% RPD for duplicate samples greater than 700 mg/kg, or a duplicate difference <200 mg/kg for results less than 700 mg/kg. 50% RPD for duplicate samples greater than 1000 mg/kg.

II. QC Requirements- Per the SOW, with the following modifications:

Solid LCS

same as *prep. blank*

As per SOW
if the CLP solid LCS is not
available, an independent liquid
LCS may be used, *Note in case narrative.*

*If the matrix spike concentration is less than 50% of the sample concentration, the 80% to 120% recovery is not mandatory.

It is intended and required that the resulting data will not be qualified by the out of control sample duplicates and matrix spikes. With careful sample preparation, homogenization, and aliquot selection, the above QC criteria should be met with minimal reanalyses and redigestions.

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Contact SMO and Region 5

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for Special Analytical Services. Should you have any questions or need any assistance, please call the Sample Management Office.

Attachments

The following ^{three} forms are mandatory. All of the information included on these forms must be included in the raw data package. *Examples of completed forms are also attached, along with an example of a case narrative.*

U.S. EPA - CLP

1

EPA Sample No.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No: _____ SAS No: _____ SDG No: _____

Date Recieved: _____ Lab Sample ID: _____

Total Sample Weight (g): _____

Weight of Dust and Fibrous Mtl (g): _____

Weight of Extraneous Material (g): _____

Weight of Suspected Paint Chips (g): _____

Concentration Units: mg/kg

	Cadmium	C	Q	Lead	C	Q
Dust						
Paint Chips*						
Composite Result						

Sample Description: _____

Comments: _____

* Paint Chips (check one):

Suspected

☐

Probable

☐

Net Sample Weights Worksheet

Analyst: _____

Date: _____

Balance Checked: _____

Sample I.D.	Chip Tare Weight (g)	Total Chip Weight (g)	Net Weight of Chips (g)	Tare Weight Ext Mtl (g)	Total Weight Ext Mtl (g)	Net Weight Ext Mtl (g)

Extraneous Material (Ext Mtl) and Chip net weights are also recorded on the sample description worksheet

U.S. EPA - CLP

1

EPA Sample No.

Lab Name: EXAMPLE_____ Contract:_____

Lab Code:_____ Case No:_____ SAS No:_____ SDG No:_____

Date Recieved:_____ Lab Sample ID:_____

Total Sample Weight (g): 4.49_____

Weight of Dust and Fibrous Mtl (g): 4.43_____

Weight of Extraneous Material (g): 0.02_____

Weight of Suspected Paint Chips (g): 0.040_____

Concentration Units: mg/kg

	Cadmium	C	Q	Lead	C	Q
Dust	36	P		5800	P	
Paint Chips*	170	F		18000	F	
Composite Result	37			5900		

Sample Description: An examination of the total sample revealed dust, carpet fibers and blue and white suspected paint chips. The suspected paint chips were separated. Plastic and plant parts were removed as extraneous materials. The remaining dust portion was ground and yielded a sample that was 50% dust and 50% lint. _____

Comments: After consulting Region 5, the Cd and Pb results for the dust sample were reported as an average of three determinations.

* Paint Chips (check one):

Suspected

☐

Probable

☒

— EXAMPLE —

U.S. EPA - CLP

1

EPA Sample No.

Lab Name: EXAMPLE _____ Contract: _____

Lab Code: _____ Case No: _____ SAS No: _____ SDG No: _____

Date Recieved: _____ Lab Sample ID: _____

Total Sample Weight (g): 27.88 _____

Weight of Dust and Fibrous Mtl (g): 25.59 _____

Weight of Extraneous Material (g): 1.74 _____

Weight of Suspected Paint Chips (g): 0.55 _____

Concentration Units: mg/kg

	Cadmium	C	Q	Lead	C	Q
Dust	8.9	P		360	P	
Paint Chips*	15	P		2900	P	
Composite Result	8.9			370		

Sample Description: The examination of the total sample revealed dust, carpet fibers and suspected paint chips. Paper, wood and plant materials were removed as extraneous materials. Some blue suspected paint chips were separated. The dust portion was ground and yielded a sample that was 90% lint and 10% dust. _____

Comments: _____

* Paint Chips (check one):

Suspected ☐

Probable ☒

EXAMPLE -

CASE NARRATIVE
NL INDUSTRIES
ICAP for Pb and Cd in dust
SF0819

Fifty nine dust samples were submitted for analysis by ICAP for Pb and also Cd.

Pre analysis preparation

Upon receipt the samples were examined under a low power stereomicroscope. Notations were made as to contents of the clear plastic bags containing the dust samples. For each sample, a total sample weight was determined and recorded. Next the sample was physically separated into fractions - a dust fraction, a suspected paint chip fraction, and an extraneous material fraction. Each fraction was weighed and the weights recorded. The dust fraction and the suspected paint chip fraction were each separately ball milled using plastic balls and containers. The extraneous materials were not milled or analyzed. Approximately half gram aliquots were taken for the dust fraction digestion. If possible, twenty to fifty milligrams of ground suspected paint chips were used for digestion. Some of the suspected paint chip samples contained less than 20 milligrams. In these cases, the entire sample was digested. The CRL SOP for soil samples using microwave digestion with nitric acid and yttrium added as an internal standard was used to prep these sample fractions. A description of the milled dust portion of each sample was included on the Form 1 report. The relative volumes of lint and dust as percentages were included in the descriptions. "Lint" is used to describe any fibrous material remaining after milling.

ICAP Analysis

Method development: Based on the analysis of samples from another site and from initial attempts at analyzing SF0819 samples, it was found that there appeared to be a stray light interference from Cu affecting the Pb 220 nm line when using the TJA 1160 ICAP unit. Cu was found at concentrations high enough to affect Pb results in a number of dust samples. A decision then was made with Dr. J. Morris to use the TJA ICAP 61 unit where this kind of interference was not observed (see attached scans illustrating this).

Based on the previous work mentioned above, an instrument run method was created for the TJA 1160 to determine Pb and Cd in digests containing yttrium as an internal standard. All the element lines selected for this method are used in the standard CRL SED5 or SED5Y run methods. The lines selected essentially used the same limits, background correction points, and calibration standards that were used for SED5Y. Other elements selected included Ca, Mg, and Na, which were to be viewed as indicators of "high solids" content; As, Al, Fe, Cu, Ti, and Mo were selected for purposes of IEC corrections.

- EXAMPLE -

CASE NARRATIVE (continued)
SF0819

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A similar run method, DUSTY61, based on this 1160 run method was created and used with the TJA ICAP 61 but additional element lines and different background correction points were selected. Selection of these points was based on previously run element scans and noted observations of these scans. For both Pb and Cd an additional line was available and selected as a "back up" line (standardized, monitored, but not reported). Pb values were reported using the 220 nm line and for Cd the 228 nm line was used. The Pb backup line was the 182 nm line and for Cd the backup was the 214 nm line. A copy of the method is included with the Case deliverables. Nitrogen gas was used to purge the torch compartment optics (a flow setting of approximately 10 psi was used).

ICAP Analyses: The actual analysis run numbers for the ICAP 61 unit were Runs 952A, 954A, 957A, 958A, 960A, 963A, 965A, 966A, and 976A. Each run was conducted on a different day. The earlier runs included prepared dust samples while the later runs included the prepared suspected paint chip samples.

Reporting of results: Since the work performed for this project can essentially be considered more experimental than routine in nature, the standard Case deliverable protocols were not entirely followed. A number of worksheet and reporting forms were designed by ESAT personnel and used for recording fraction weights, sample observations, and reporting of sample results for Pb and Cd.

Where appropriate, a composite value was reported for each sample for Pb and for Cd. The composite value was calculated by combining the dust fraction concentration and the suspected paint chip fraction concentration.

Per discussion with D. Payne and Dr. J. Morris, additional data reports were to be provided for the data user. These reports included results for digestion blanks, laboratory duplicates, matrix spikes, and laboratory control samples (LCS). For these latter reports, copies of the CRL ENABLE report forms designed by M. Jupp were utilized.

Comments: During the course of preparation of some of the suspected paint chips, the plastic grinding balls were inadvertently included. These prepared sample fractions were analyzed using GFAA; this was so noted on the report forms for the affected samples.

- EXAMPLE -

CASE NARRATIVE (continued)
SF0819

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Pb results for the NBS reference paint sample show low extraction (digestion) efficiency (50% and 73% Pb recovery). However, even with this lower extraction value the overall effect on the composite value was minimal to insignificant for the samples analyzed since the amount of paint chip material was small compared to the dust sample fraction. It should also be pointed out that throughout all the runs conducted, the LCS results were consistently (with one exception) within the control ranges specified by EMSL documentation for the LCS used. Even though the EMSL values may not necessarily reflect "true" values they do represent a comparative indicator of extraction efficiency.

Spex stock standards (1000 ug/ml and 10,000 ug/ml) were used to prepare working standards. Custom made solutions from Inorganic Ventures were used to prepare working check solutions. For the first seven analysis runs, the CRL 5 ppm AQC check solution made from Spex sources was used as the primary control check standard. For the last two analysis runs, a 5 ppm AQC solution prepared from the Inorganic Ventures solutions was used as the primary control check standard.

Because of the separation method used to split the sample into separate portions or fractions, it was found that some samples were found to yield heterogeneous fractions, even after attempting homogenization of the fractions by grinding/mixing in a laboratory ball mill. This was evidenced from the large RPD values for laboratory duplicates while many spiked samples showed acceptable matrix spike recovery. For a few samples, then, triplicate determinations were performed and average results were reported.

Although no formal report forms were provided with the Case deliverables, the additional information from the two back up element lines (the Pb 182 nm and the Cd 214 nm line) agreed with the Pb and Cd values reported. Overall, the corresponding element values agreed within 2% to 4%.

A one day check of IDL values for the Pb and Cd lines was conducted during analysis Run 966A. A table listing these values is included with the Case deliverables. These IDL values are in line (i.e., they agree) with values obtained from earlier TJA 61 studies.

EXAMPLE -